Air Resources Board

Barbara Riordan, Chairman

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MEMORANDUM

TO: Peter Venturini, Chief
Stationary Source Division

FROM: Terry McGuire, Chief
Planning & Technical Support Division

DATE: January 19, 1999

SUBJECT: ATMOSPHERIC CONDITIONS WHICH FAVOR NEGATIVE HYDROCARBON REACTIVITY

Attached is a paper entitled *NO_x Concentrations and VOC/NO_x Ratios in California* which discusses the Dunn-Edwards issue regarding negative hydrocarbon reactivity.

This paper affirms that Dunn-Edwards is correct in that when NO_x concentrations are very low and VOC/NO_x ratios are very high, many hydrocarbons exhibit negative reactivities. The paper goes on to examine recent prevailing air quality conditions in the California air basins which experience ozone problems and finds that such NO_x and VOC/NO_x conditions are almost non-existent.

If you have questions regarding this matter, please contact Luis Woodhouse at 322-6156.

Attachment

cc: Luis Woodhouse

NO_x Concentrations and VOC/NO_x Ratios in California

January 19, 1999

Introduction

Dunn-Edwards Corporation (DEC) has provided the California Air Resources Board (CARB) with the results of research conducted by Dr. William Carter, using box-model simulations and the SAPRC-97 chemical mechanism. The research looked at the influence of nitrogen oxide (NO_x) concentrations on the incremental reactivity (IR) of selected volatile organic compounds (VOCs). The VOCs studied were n-octane, ethanol, m-xylene, toluene, and an urban ROG mixture. The NO_x concentrations used in the research ranged from 1 ppb up to 40 ppb, with the VOC/NO_x ratios of up to 80. Dr. Carter showed that as the NO_x concentration is reduced, or, equivalently, as the VOC/NO_x ratio increases, the reactivity of the VOCs decreases and can become negative. This research also shows that as NO_x increases the IR will increase and eventually become positive for all VOCs studied. However, note that the chemical mechanism used in the DEC study has not been adequately evaluated at these low NO_x concentrations (Carter, 1998).

The DEC study confirms that the IR of organic compounds depends on the environmental conditions, particularly on NO_x availability. For example, when the initial NO_x concentration is 20 ppb, m-xylene shows negative IRs at VOC/NO_x ratios of 30 and above. When the initial NO_x concentration is 5 ppb, m-xylene shows negative IRs at VOC/NO_x ratios of 40 and above. Toluene, n-octane and the Urban ROG mixture show negative IRs at lower VOC/NO_x ratios. At 1 ppb or less of initial NO_x, all VOCs studied, except ethanol, had negative IRs at all VOC/NO_x ratios.

The data conclusions by DEC are based on sound scientific research and agree with the results of other research (Carter *et al.*, 1994), confirming the IR dependence on the VOC/NO_x ratio, and showing that at very low NO_x concentrations the IR can become negative as the VOC/NO_x ratio increases. At low NO_x concentrations, the removal of NO_x by reactions with VOCs to form nitrogen-containing products become very important and can have negative effects on the formation of ozone. In addition, at very low NO_x concentrations, radical-radical termination reactions will be enhanced which will retard the generation of ozone (Bergin, *et al.*, 1998).

Ambient NMOC/NO_x Ratios

Ambient NMOC/NO_x ratios (NMOC stands for nonmethane organic compounds) are calculated using data collected in the early morning, 6-9 a.m., of a given day. This ratio is an indicator of the ambient ozone precursors before the photochemical reactions that generate smog take place, and it is similar, in concept, to the initial NMOC/NO_x ratio that is used to characterize a smog chamber before the start an experiment (i.e., before the air sample is irradiated). However, the 6-9 a.m. NMOC/NO_x ratio does not represent the complexities of ozone formation, such as the effect of pollutant transport, in California air basins. We used air quality data obtained from the Photochemical Assessment Monitoring Stations, PAMS, to calculate 6-9 a.m. $NMOC/NO_x$ ratios in California. The PAMS monitoring network provides for improved sampling procedures, better data quality control, and, also, speciation of NMOC. Data used in this analysis were from the summers of 1996 and 1997 (the most recent data available after the statewide introduction of cleaner burning gasoline), and they are summarized in Tables A and B for selected sites.

According to the information provided by DEC, the Urban ROG mix, which is used to represent ambient air in smog chamber experiments, had a negative reactivity at a $NMOC/NO_x$ ratio of 20 or greater, and NO_x concentrations between 5-40 ppb. We calculated the percent of ambient air samples that had both a NO_x concentration of 40 ppb, or less, and a $NMOC/NO_x$ ratio of 20, or greater, and they are summarized in Table C.

The information shown in Tables A, B, and C demonstrate that the NO_x concentrations and $NMOC/NO_x$ ratios used in the DEC study are not typical of the ambient conditions of California. For example, during the summers of 1996 and 1997, the average $NMOC/NO_x$ ratio is below 15 for all the sites studied. The percent of samples that had a NO_x concentration of 40 ppb, or less, and a $NMOC/NO_x$ ratio of 20, or greater, is 0 to 4 percent at most sites. The monitoring stations in Sacramento Del Paso Manor and Arvin had only 10 percent of the samples with ratios over 20, together with a NO_x concentration of 40 ppb, or less. The Los Angeles North Main Street monitoring site, situated in the air basin with the worst pollution problem in California, had an average $NMOC/NO_x$ ratio of about 5, with the maximum ratio not exceeding a value of 10.

Conclusions

The data presented by DEC is based on sound scientific research, however, air quality typical of California shows that NO_x concentrations are dramatically greater and $NMOC/NO_x$ ratios are almost always lower than those that result in negative IRs.

References

Bergin, M. S., A. G. Russell, W.P.L. Carter, B. E. Croes, and J.H. Seinfeld, "*VOC Reactivity and Urban Ozone Control.*" Encyclopedia of Environmental Analysis and Remediation, 1998.

Carter, W.P.L. D. Luo, I. L. Malkina, and J. A. Pierce, "*Environmental Chamber Studies of Atmospheric Reactivities of Volatile Organic Compounds. Effects of Varying ROG and NO_x.*" Final Report to Coordinating Council, Inc., California Air Resources Board, South Coast Air Quality Management District. September 10, 1994.

Carter, W.P.L., personal communication to L. Woodhouse (November, 1998).

Table A
NMOC to NO_x Ratio (6-9 AM) from Selected Sites in California
(Summers 1996 and 1997)

Site	Average	Minimum	Maximum	Std. Dev.
Fresno –1st Street	6.2	3.5	13.6	2.0
Parlier	6.4	3.7	14.3	1.8
Clovis –N Villa Avenue	8.6	3.0	100.7	12.0
Bakersfield –Golden State Hwy	6.9	3.0	19.4	2.6
Arvin –Bear Mountain Blvd.	14.8	2.6	243.3	33.6
Los Angeles –North Main Street	4.6	1.6	9.5	1.8
Sacramento –Del Paso Manor	13.7	3.8	160.5	22.5
Elk Grove –Bruceville Road	7.9	1.7	35.4	5.9
Folsom –Natoma Street	7.8	2.0	20.4	4.0
San Diego –12th Street	7.7	2.2	35.3	6.3

Table B
NO_x Concentrations[a] (6-9 AM) from Selected Sites in California
(Summers 1996 and 1997)
-ppb-

Site	Average	Minimum	Maximum	Std. Dev.
Fresno –1st Street	49	11	140	29
Parlier	31	13	53	10
Clovis –N Villa Avenue	36	8	102	18
Bakersfield –Golden State Hwy	69	16	142	32
Arvin –Bear Mountain Blvd.	20	5	54	10
Los Angeles –North Main Street	145	15	325	95
Sacramento –Del Paso Manor	25	1	95	20
Elk Grove –Bruceville Road	17	2	47	12
Folsom –Natoma Street	17	4	38	9
San Diego –12th Street	45	6	170	33

a) Data for this table corresponds to days with available NMOC data. Data for days with no NMOC were not included

Table C
Percent of Samples (6-9 a.m.) with
Ambient NO_x Concentration Less Than or Equal to 40 ppb,
and NMOC/NO_x Ratio Greater Than or Equal to 20
For Selected Sites in California
(Summers of 1996 and 1997)

Monitoring Site	Percent
Fresno –1st Street	0
Parlier	0
Clovis –N Villa Avenue	2
Bakersfield –Golden State Hwy	0
Arvin -Bear Mountain Blvd.	10
Los Angeles –North Main Street	0
Sacramento –Del Paso Manor	12
Elk Grove –Bruceville Road	4
Folsom –Natoma Street	3
San Diego –12th Street	4